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A Novel Reaction of 1-Aryl-2-bromodiazene 1-Oxides with Alkenes

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1-Aryl-2-bromodiazene 1-oxides are able to react with terminal alkenes CH_2=CHR to produce 1-(2-bromo-2-*R*-ethyl)-2-aryldiazene 2-oxides which can be easily converted into 1-(α,β-unsaturated)-2-aryldiazene 2-oxides by treatment with triethylamine.

Our previous communication reported a simple method of preparation of the previously unknown *N*-bromodiazene oxides (NBD) which consisted of the reaction of nitrosobenzenes with tribromoamine. the latter was generated *in situ* by passing gaseous ammonia through a suspended brominating agent (*N*-bromosuccinimide or *N*,*N*-dibromoisocyanurate) at −60 °C.[1] In the present communication we report that the improved technique allows us to carry out the process at −10→0 °C using NH_4Br instead of ammonia.

Reactions of diazene 1-oxides which result in the replacement of one N-2 substituent by another are rather unusual.[2] NBD are thought to widen the scope of such reactions.

The reaction of NBD with the terminal bonds of alkenes has been observed, the diazene oxide group being connected to the unsubstituted carbon atom and bromine to the substituted one. The reaction is electrophilic in character, the rate being fastest with electron-rich alkenes. When ethylvinyl ether was used the reaction was complete after 30 min at −15 °C, styrene required 2 h at 40 °C and in the case of hex-1-ene the reaction did not take place at all under the same conditions. However, the rate was greatly increased by the addition of hydroperoxides to

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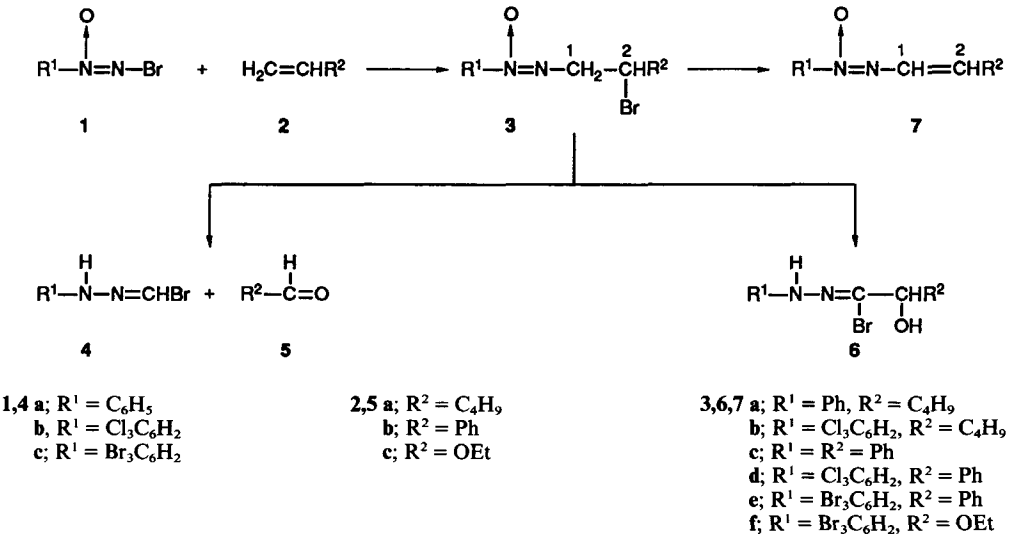

1,4 a; $R^1 = C_6H_5$
b, $R^1 = Cl_3C_6H_2$
c; $R^1 = Br_3C_6H_2$

2,5 a; $R^2 = C_4H_9$
b; $R^2 = Ph$
c; $R^2 = OEt$

3,6,7 a; $R^1 = Ph$, $R^2 = C_4H_9$
b; $R^1 = Cl_3C_6H_2$, $R^2 = C_4H_9$
c; $R^1 = R^2 = Ph$
d; $R^1 = Cl_3C_6H_2$, $R^2 = Ph$
e; $R^1 = Br_3C_6H_2$, $R^2 = Ph$
f; $R^1 = Br_3C_6H_2$, $R^2 = OEt$

Scheme 1

Table 1 Diazene oxides **3a,b,d,e** and **7a,b,d,e** from NBD **1a,b,c** and alkenes **2a,b** (Scheme 1)

Starting compounds		Compound3	Compound 7
1 = R^1	**2** = R^2	% Yield[a]	% Yield[b] (*E*:*Z*)[c]
a Ph	**a**[d] C_4H_9	**a**[e] 58 (45)	**a** 98 (50:50)
b $Cl_3C_6H_2$	**a**[d] C_4H_9	**b**[e] 63	**b** 96 (60:40)
b $Cl_3C_6H_2$	**b**[f] Ph	**d**[g] 81	**d** 95 (95:5)
c $Br_3C_6H_2$	**b**[f] Ph	**e**[g] 97 (90)	**e** 98 (85:15)

[a] ^{1}H NMR yield determined with an internal standard based on **1**, isolated yield in parentheses. [b] Isolated yield based on **3**. [c] Determined by 300 MHz ^{1}H NMR. [d] 300% excess, 0.05 mol dm^{-3} hydroperoxides. [e] *Conditions*: 40 °C, 8 h. [f] 300% excess. [g] *Conditions*: 40 °C, 2 h.

Table 2 Decomposition of diazene oxides **3** to products **4** and **5** or **6** (Scheme 1)

Starting compounds	Reaction conditions	Products, % Yield[a] 4	5	6
1a + **2b**[b]	45 °C, 1 h	**a** 0	**b** 26[c]	**c** 0
1c + **2c**[b]	CH_2Cl_2, − 15 °C, 0.5 h	**c** 89[c]	**c** 71[c]	**f** 0
3d	$CHCl_3$, saturated soln., room temp., 6 days	**b** 31	**b** 35	**d** (58)
3e	$CHCl_3$ saturated soln., room temp., 6 days	**c** 27	**b** 30	**e** (55)
	SiO_2, no solvent room temp., 1 h	**c** (65)	**b** 70	**e** 0

[a] ^{1}H NMR yield determined with internal standard based on **1** or **3**, isolated yield in parentheses. [b] **1**:**2** = 1 mol: 2 mol. [c] Based on **1**.

hex-1-ene (Table 1). This fact allows us to propose that the reaction is a radical one. The structure of addition product **3** suggests that the diazene oxide radical reacts with the terminal atom of the alkene as the first stage and the resulting radical tears off a bromine atom from another NBD molecule.

The stability of product **3** depends upon the nucleophilicity of the oxygen atom of the diazene oxide group (which is determined by substituent R^1) and on the mobility of the bromine atom (which is determined by substituent R^2). Compounds **3a,b,d,e** are stable enough to be isolated and characterized by spectroscopic methods. The treatment of these compounds with triethylamine resulted in α,β-unsaturated diazene oxides **7** as two isomers. In the case of R^2 = Ph the *trans* isomer (relative to the C = C double bond) predominates (Scheme 1, Table 1). The chemistry of this class of compounds is practically unknown.[3]

Since compound **3f** (R^2 = OEt) was too unstable to be isolated due to the high lability of the bromine atom, the reaction of NBD **1c** with ethylvinyl ether resulted in hydrazone **4c** and ethyl formate. These products are thought to be formed during the decomposition of the intermediate salt **8**, resulting from the cyclization of molecule **3f** (Scheme 2).

The decomposition of compound **3c** proceeded faster than that of **3d,e** due to the greater nucleophilicity of the oxygen atom in the diazene oxide, the rate of decomposition being comparable with the rate of reaction of NBD **1a** with styrene. As a result the reaction yielded a complex mixture of products, excluding hydrazone **4a**.

Compounds **3d,e** decomposed in solution within a few days at room temperature, giving compound **6** as the major product of the reaction (Table 2). We suggest that this compound is formed during the retrocyclization of intermediate **8** along the N–O bond. However, decomposition may also lead to hydrazone **4** and benzaldehyde. This process took place when **3d** and **e** were maintained on silica gel for 1 h at room temperature.

All new compounds were characterized by ^{1}H NMR (300 MHz), ^{13}C NMR (75.43 MHz), ^{14}N NMR (21.69 MHz) (Table 3), IR and MS. Satisfactory elemental analyses were obtained for **4b,c**; **6d,e**; **7d,e**.

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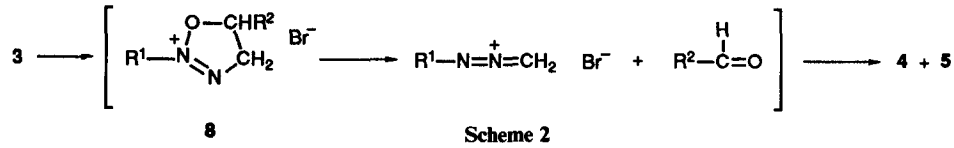

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Scheme 2

Table 3 Selected NMR data for some new compounds (solutions in $CDCl_3$).

Compound	^{13}C NMR, δ		^{1}H NMR, δ, *J*/Hz		^{14}N MNR δ/ppm (Me NO_2) ($\Delta\upsilon_{0.5}$/Hz)
	C(1)	C(2)	HC(1)	HC(2)	
3a	59.47	52.16	H_A 4.05, H_B 4.10 J_{AB} = 19.2, J_{AM} = 6.0,	H_M 4.43 J_{BM} = 6.4	− 50(150)
3e	59.72	48.94	H_A 4.42, H_B 4.47 J_{AB} = 18.6, J_{AM} = 6.8,	H_M 5,46 J_{BM} = 7.8	− 52(250)
7a	131.29 133.86	138.05 140.41 } *Z,E*	*Z*: 7.91, *J* = 13.7 *E*: 7.78, *J* = 8.2	Z: 6.60 E: 5.94	− 65.3(130)
7e	131.36	138.43,*Z*	*Z*: 8.56, *J* = 14.0 *E*: 7.84, *J* = 11.1	Z: 7.35 E: 6.70	− 67.8(140)
6e	126.71	77.79	—	5.5	—